

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C. 20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 11 October 2000 (11.10.00)	
International application No. PCT/EP00/01275	Applicant's or agent's file reference MBJ-0361
International filing date (day/month/year) 15 February 2000 (15.02.00)	Priority date (day/month/year) 15 February 1999 (15.02.99)
Applicant YAGUCHI, Minoru et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

08 September 2000 (08.09.00)

☐ in a notice effecting later election filed with the International Bureau on:
2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference MBJ-0361	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/01275	International filing date (day/month/year) 15/02/2000	Priority date (day/month/year) 15/02/1999
International Patent Classification (IPC) or national classification and IPC C04B24/26		
Applicant MBT HOLDING AG et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 08/09/2000	Date of completion of this report 05.06.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Rauscher, M Telephone No. +49 89 2399 8566 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/01275

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-3,5,7-12	as originally filed	
4,6	with telefax of	15/05/2001

Claims, No.:

1,2,3 (part),11	as originally filed	
3 (part),4-10	with telefax of	15/05/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/01275

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-11
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/01275

AS TO SECTION V:

1. The following documents have been considered:

D1: EP-A-0 850 894 (NIPPON CATALYTIC CHEM IND) 1 July 1998 (1998-07-01)

D2: DE 41 42 388 A (SANDOZ AG) 2 July 1992 (1992-07-02)

D1 discloses a cement additive, comprising a copolymer having units derivable from polyalkylene glycol ethers of unsaturated alcohols and units derivable from maleic acids species (see page 3 and claim 1).

The copolymers may have additional components such as esters of unsaturated acids and polyalkylene glycols (see page 6, lines 28-49).

These copolymers may be blended with polyalkylene glycol derivatives (antifoaming agents) in amounts of up to 10 wt% of the copolymer (see page 8, line 21 -59 and page 9, line 24 -32).

D2 describes similar copolymers having units of esters such as mentioned above together with derivatives of unsaturated acids and styrene.

2. It follows from the discussion of the relevant prior art that the additive of claims 1-3 is not novel.

The molecular weight of the copolymers, the ratio of components within the copolymer and moreover their amounts to be added to a cementitious composition as set out in present claims 4-8 and 10 and 11 are known as well from D1 (see page 1, lines 46-48; page 3, line 18; page 9, line 24-29).

The feature of steam curing mentioned in claim 9 was not found in D1. However the wording "...concrete..for ...steam curing..." cannot install novelty.

3. It seems, that the optional component (D) mentioned in claim 3 is not mentioned in D1.

Presently it is not to be seen that incorporation of this component results in a remarkable technical effect.

4. It is noted that the upper limit of 10% of the polyalkylene glycol component of the

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/01275

blend coincides with the lower limit of 10% introduced with the amended claims.
Therefore this amendment does not install novelty.

Apart from that such an amendment cannot be allowed under Article 34(2)(b),

- since it introduces the teaching of a new technical effect which is achieved when applying at least amounts as now indicated
- since such new teaching touches the matter of inventive step
- and since this teaching is not part of the original disclosure.

In order to overcome this objection a lower limit of 15% as indicated in examples may be introduced in a new main claim.

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference MBJ-0361	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 00/ 01275	International filing date (day/month/year) 15/02/2000	(Earliest) Priority Date (day/month/year) 15/02/1999
Applicant MBT HOLDING AG et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/01275

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B24/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 850 894 A (NIPPON CATALYTIC CHEM IND) 1 July 1998 (1998-07-01) page 2, line 33 -page 6, line 49 page 9, line 33 - line 44	1-11
A	DE 41 42 388 A (SANDOZ AG) 2 July 1992 (1992-07-02) page 2, line 5 -page 3, line 57	1,8,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

16 May 2000

Date of mailing of the international search report

24/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Authorized officer

Rauscher, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/01275

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0850894	A	01-07-1998	BR 9706470 A	08-06-1999
			JP 10236857 A	08-09-1998
			US 5912284 A	15-06-1999
			JP 10236858 A	08-09-1998
DE 4142388	A	02-07-1992	AT 405934 B	27-12-1999
			AT 251591 A	15-05-1999
			CH 682237 A	13-08-1993
			FR 2671090 A	03-07-1992
			IT 1250077 B	30-03-1995
			JP 2766807 B	18-06-1998
			JP 6211940 A	02-08-1994
			NO 301125 B	15-09-1997
			SE 506652 C	26-01-1998
			SE 9103844 A	30-06-1992
			US 5612396 A	18-03-1997

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

Mcstea, John Anthony
MBT (SCHWEIZ) AG
Patents and Trade Marks
Vulkanstrasse 110
CH-8048 Zürich
SUISSE

EINGEGANGEN

07. Juni 2001

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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year)

05.06.2001

Applicant's or agent's file reference
MBJ-0361

IMPORTANT NOTIFICATION

International application No.
PCT/EP00/01275

International filing date (day/month/year)
15/02/2000

Priority date (day/month/year)
15/02/1999

Applicant

MBT HOLDING AG et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



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Authorized officer

Koutsoftas, P

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100,000 (all molecular weights (MW) referred to herein were measured by gel permeation chromatography with polyethylene glycol as standard).

5 The invention also relates to the abovementioned cement additive, wherein the average molecular weight of the polyalkylene glycol derivatives is from 1,000-100,000, in which the alkylene is one or more C_2-C_4 species, and the terminal groups of the polyalkylene glycol is hydrogen or a C_1-C_{18} alkyl or phenyl group.

10 Further, the invention relates to the abovementioned cement additive containing 100 weight parts of the polycarboxylic acid type copolymers and 10-50 weight parts of the polyalkylene glycol derivatives.

15 Also, the invention relates to the abovementioned cement additive, wherein the amount of the polycarboxylic acid type copolymers added to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivatives added to cement is 0.005-0.5 % by weight based on the weight of cement.

20 Further, the invention relates to use of the abovementioned cement additive in high strength concrete.

The invention also relates to the use of the abovementioned cement additive in the formation of pre-formed concrete articles by steam curing.

25 The invention further provides a method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive as hereinabove described.

30 The invention further provides a method of preparation of a concrete mix adapted to be used for the manufacture of articles by steam curing, comprising the incorporation in the mix of a cement additive as hereinabove described.

In a cement additive according to the invention, the monomers (A) are typically compounds according to the abovementioned general formula (1), more specifically, the

Specific examples include styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid butyl ester, methacrylic acid methyl ester, methacrylic acid ethyl ester, methacrylic acid butyl ester, maleic anhydride, maleic acid methyl monoester, maleic acid ethyl monoester, maleic acid methyl diester, maleic acid ethyl diester, vinyl acetate, acrylamide, acrylamide methylpropansulfonic acid and/or the salts thereof, methallyl sulfonic acid and/or the salts thereof. One or more species of these may be used.

Specific non-limiting examples of polycarboxylic acid type copolymers are those described in JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858.

The composition ratio of the monomers (A) and (B) in the polycarboxylic acid type copolymers in the invention to total amount of the monomers is preferably 30-100 mole %, and the average molecular weight is preferably 3,000-100,000.

In the polyalkylene glycol derivatives of the invention, the average molecular weight is 1,000-150,000, preferably 1,000-100,000, more preferably 4,000-50,000, the alkylene is one or more C_2-C_4 species, and it may be block or random in the case of 2 or more species, the terminal groups of polyalkylene glycol are hydrogen, C_{18} maximum alkyl or phenyl groups.

In a cement additive of the invention, the preferred proportions are 100 weight parts of polycarboxylic acid type copolymers and 10-50 weight parts of polyalkylene glycol derivatives.

A cement additive of the invention is preferably used in such a quantity that polycarboxylic acid type copolymers are present in the proportion 0.05-1.0 % by weight based on cement weight and polyalkylene glycol derivatives are present in the proportion 0.005-0.5 % by weight based on cement weight. However, the amount of the cement additive according to the invention to be used can be appropriately determined according to a cement composition used, it basically being the amount which is necessary to attain the desired strength development and improved time to form removal after steam curing,

wherein R^{15} , R^{16} , R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; $R^{17}O$ is one or more species of C_2-C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

4. A cement additive according to any one of claims 1-3, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid type copolymer are 30-100 mole % based on the total mole amount of their monomers, and the average molecular weight of said polycarboxylic acid type copolymer is from 3,000 to 100,000.

5. A cement additive according to any one of claims 1-3, wherein the average molecular weight of the polyalkylene glycol derivative is from 1,000 to 100,000, and in which the alkylene is one or more C_2-C_4 species, and the terminal group of the polyalkylene glycol is hydrogen, a C_1-C_{18} alkyl group or a phenyl group.

6. A cement additive according to any one of claims 1-5, containing 100 weight parts of the polycarboxylic acid type copolymer and 10-50 weight parts of the polyalkylene glycol derivative in the mixing proportion.

7. A cement additive according to any one of claims 1-6, wherein the amount used in a cementitious composition is such that the amount of polycarboxylic acid type copolymer to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivative to cement is 0.005-0.5 % by weight based on the weight of cement.

8. A high-strength concrete mix, comprising a cement additive according to any one of claims 1-7.

9. A concrete mix for the production of articles by steam curing, comprising a cement additive according to any one of claims 1-7.

10. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.

100,000 (all molecular weights (MW) referred to herein were measured by gel permeation chromatography with polyethylene glycol as standard).

5 The invention also relates to the abovementioned cement additive, wherein the average molecular weight of the polyalkylene glycol derivatives is from 1,000-100,000, in which the alkylene is one or more C_2 - C_4 species, and the terminal groups of the polyalkylene glycol is hydrogen or a C_1 - C_{18} alkyl or phenyl group.

10 Further, the invention relates to the abovementioned cement additive containing 100 weight parts of the polycarboxylic acid type copolymers and 10-50 weight parts of the polyalkylene glycol derivatives.

15 Also, the invention relates to the abovementioned cement additive, wherein the amount of the polycarboxylic acid type copolymers added to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivatives added to cement is 0.005-0.5 % by weight based on the weight of cement.

20 Further, the invention relates to use of the abovementioned cement additive in high strength concrete.

The invention also relates to the use of the abovementioned cement additive in the formation of pre-formed concrete articles by steam curing.

25 The invention further provides a method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive as hereinabove described.

30 The invention further provides a method of preparation of a concrete mix adapted to be used for the manufacture of articles by steam curing, comprising the incorporation in the mix of a cement additive as hereinabove described.

In a cement additive according to the invention, the monomers (A) are typically compounds according to the abovementioned general formula (1), more specifically, the

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ART 34 AMDT

Specific examples include styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid butyl ester, methacrylic acid methyl ester, methacrylic acid ethyl ester, methacrylic acid butyl ester, maleic anhydride, maleic acid methyl monoester, maleic acid ethyl monoester, maleic acid methyl diester, maleic acid ethyl diester, vinyl acetate, acrylamide, acrylamide methylpropanesulfonic acid and/or the salts thereof, methallyl sulfonic acid and/or the salts thereof. One or more species of these may be used.

Specific non-limiting examples of polycarboxylic acid type copolymers are those described in JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858.

The composition ratio of the monomers (A) and (B) in the polycarboxylic acid type copolymers in the invention to total amount of the monomers is preferably 30-100 mole %, and the average molecular weight is preferably 3,000-100,000.

In the polyalkylene glycol derivatives of the invention, the average molecular weight is 1,000-150,000, preferably 1,000-100,000, more preferably 4,000-50,000; the alkylene is one or more C₂-C₄ species, and it may be block or random in the case of 2 or more species, the terminal groups of polyalkylene glycol are hydrogen, C₁₈ maximum alkyl or phenyl groups.

In a cement additive of the invention, the preferred proportions are 100 weight parts of polycarboxylic acid type copolymers and 10-50 weight parts of polyalkylene glycol derivatives.

A cement additive of the invention is preferably used in such a quantity that polycarboxylic acid type copolymers are present in the proportion 0.05-1.0 % by weight based on cement weight and polyalkylene glycol derivatives are present in the proportion 0.005-0.5 % by weight based on cement weight. However, the amount of the cement additive according to the invention to be used can be appropriately determined according to a cement composition used, it basically being the amount which is necessary to attain the desired strength development and improved time to form removal after steam curing.

REPLACED BY
ART 34 AMDT

wherein R^{15} , R^{16} , R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; $R^{17}O$ is one or more species of C_2 - C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

4. A cement additive according to any one of claims 1-3, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid type copolymer are 30-100 mole % based on the total mole amount of their monomers, and the average molecular weight of said polycarboxylic acid type copolymer is from 3,000 to 100,000.
5. A cement additive according to any one of claims 1-3, wherein the average molecular weight of the polyalkylene glycol derivative is from 1,000 to 100,000, and in which the alkylene is one or more C_2 - C_4 species, and the terminal group of the polyalkylene glycol is hydrogen, a C_1 - C_{18} alkyl group or a phenyl group.
6. A cement additive according to any one of claims 1-5, containing 100 weight parts of the polycarboxylic acid type copolymer and 10-50 weight parts of the polyalkylene glycol derivative in the mixing proportion.
7. A cement additive according to any one of claims 1-6, wherein the amount used in a cementitious composition is such that the amount of polycarboxylic acid type copolymer to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivative to cement is 0.005-0.5 % by weight based on the weight of cement.
8. A high strength concrete mix, comprising a cement additive according to any one of claims 1-7.
9. A concrete mix for the production of articles by steam curing, comprising a cement additive according to any one of claims 1-7.
10. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.

REPLACED BY
ART 34 AMLE



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C04B 24/26	A1	(11) International Publication Number: WO 00/48961 (43) International Publication Date: 24 August 2000 (24.08.00)
<p>(21) International Application Number: PCT/EP00/01275</p> <p>(22) International Filing Date: 15 February 2000 (15.02.00)</p> <p>(30) Priority Data: 11/35350 15 February 1999 (15.02.99) JP</p> <p>(71) Applicant (for all designated States except US): MBT HOLD- ING AG [CH/CH]; Vulkanstrasse 110, CH-8048 Zürich (CH).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): YAGUCHI, Minoru [JP/JP]; 2722, Hagizono, Chigasaki-shi, Kanagawa-ken (JP). NAGAMINE, Hidenori [JP/JP]; 2722, Hagizono, Chigasaki-shi, Kanagawa-ken (JP). KANEI, Keita [JP/JP]; 2722, Hagizono, Chigasaki-shi, Kanagawa-ken (JP).</p> <p>(74) Agent: MCSTEAL, John, Anthony; MBT (Schweiz) AG, Patents and Trade Marks, Vulkanstrasse 110, CH-8048 Zürich (CH).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>
(54) Title: CEMENT ADDITIVE		
<p>(57) Abstract</p> <p>A cement additive comprising a polycarboxylic acid type copolymer and/or a salt thereof and a polyalkylene glycol derivative, wherein said polycarboxylic acid type copolymer contains one or more species of copolymers composed of at least an unsaturated polyalkylene glycol type monomer and an unsaturated mono- or dicarboxylic acid type monomer as their monomer components. Concretes in which the additive is used have excellent flow, without significant retarding effect, and a low air entrainment. When used with concrete for steam curing, it allows earlier removal of form work.</p>		

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Cement Additive

This invention relates to a cement additive and more particularly, to a cement additive used to improve the fluidity and appearance of strength of cement slurry, cement
5 paste, mortar and concrete.

Various cement additives comprising polycarboxylic acid type copolymers have been proposed for enhancing the fluidity and flowability of concrete. While this works well for ordinary concretes, it is not so effective when high strength and high durability are
10 required, as such copolymers tend to entrain an excess of air and retard setting.

In relation to pre-formed concrete products, it is strongly desired to decrease the total time spent in a form and to prevent defects when the form is removed. For such products, good appearance is also highly desirable, when the form is removed after steam curing.
15 Various polycarboxylate materials to achieve this have been proposed, but none have been entirely satisfactory, causing such problems as retarded setting and low fluidity.

It has now been found that a cement additive containing a polycarboxylic acid type copolymer and a polyalkylene glycol derivative having a specific molecular structure can
20 alleviate and sometimes completely remove all the above-mentioned problems, by having a high dispersing ability for various concretes, improving and retaining the fluidity of concrete, and also making it possible to increase the strength of pre-formed concrete, such that form removal after steam curing can be carried out relatively early, giving a product with low aeration.

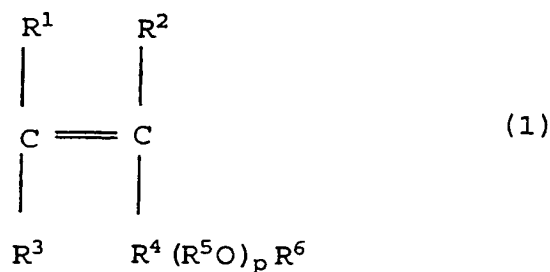
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The invention therefore provides a cement additive containing a polycarboxylic acid type copolymer and/or the salts thereof and a polyalkylene glycol derivative, said polycarboxylic acid type copolymer contains at least one species of copolymer, the monomers of which copolymer comprise at least an unsaturated polyalkylene glycol type
30 monomer (A) and an unsaturated mono- or dicarboxylic acid type monomer (B).

The invention also relates to a cement additive, wherein the polycarboxylic acid type copolymers are copolymers which additionally include as monomer components an

unsaturated polyalkylene glycol ester type monomer (C) and/or a monomer (D) polymerizable with the above-mentioned monomers (A) and (B), or with the monomers (A), (B) and (C).

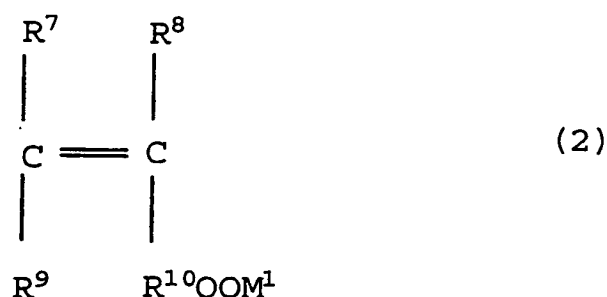
- 5 The invention further relates to the above-mentioned cement additive, wherein the monomer (A) is a compound according to the general formula (1):



- 10 wherein R^1 , R^2 and R^3 are each independently hydrogen or methyl, provided that not all are methyl; R^4 is $-\text{CH}_2\text{O}-$, $-(\text{CH}_2)_2\text{O}-$, $-\text{C}(\text{CH}_3)_2\text{O}-$ or $-\text{O}-$; the total carbon number of R^1 , R^2 , R^3 and R^4 is 3; $R^5\text{O}$ is one or more species of C_2 - C_4 oxyalkylene groups, and in the case of two or more species may be block or random; R^6 is hydrogen or a C_1 - C_{22} alkyl, phenyl or C_1 - C_{18} alkylphenyl group; p is an integer from on average 1 to 100;

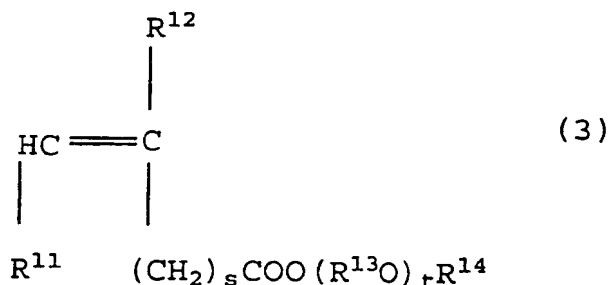
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the monomer (B) is a compound according to the general formula (2):



- 20 wherein R^7 and R^8 are each independently hydrogen or methyl; R^9 is hydrogen, methyl or $-(\text{CH}_2)_q\text{COOM}^2$; R^{10} is $-(\text{CH}_2)_r-$; q and r are each independently an integer from 0 to 2; M^1 and M^2 are a monovalent metal, a divalent metal, ammonium or an organic amine;

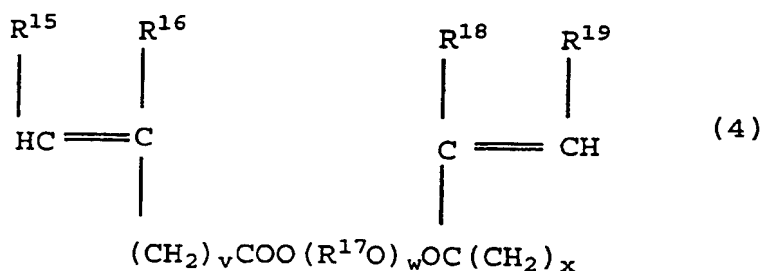
the monomer (C) is a compound according to the general formula (3):



- 5 wherein R^{11} and R^{12} are each independently hydrogen, methyl or $(\text{CH}_2)_u\text{COOM}^3$, u is an integer from 0 to 2, M^3 is a monovalent metal, a divalent metal, ammonium or an organic amine; R^{13}O is one or more species of C_1 - C_4 oxyalkylene groups, and in the case of two or more species may be block or random; R^{14} is hydrogen or a C_1 - C_{22} alkyl, phenyl or C_1 - C_{22} alkylphenyl group; s is an integer from 0 to 2; t is an integer an average from 1 to 300; and

10

the monomer (D) is a compound according to the general formula (4):



- 15 wherein R^{15} , R^{16} , R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; R^{17}O is one or more species of C_2 - C_4 oxyalkylene groups, and in the case of two or more species may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

20

The invention also relates to the abovementioned cement additive, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid-type copolymers are 30-100 mole % based on the total mole amount of the monomers, and the average molecular weight of said polycarboxylic acid-type copolymer is from 3,000-

100,000 (all molecular weights (MW) referred to herein were measured by gel permeation chromatography with polyethylene glycol as standard).

5 The invention also relates to the abovementioned cement additive, wherein the average molecular weight of the polyalkylene glycol derivatives is from 1,000-100,000, in which the alkylene is one or more C_2 - C_4 species, and the terminal groups of the polyalkylene glycol is hydrogen or a C_1 - C_{18} alkyl or phenyl group.

10 Further, the invention relates to the abovementioned cement additive containing 100 weight parts of the polycarboxylic acid type copolymers and 5-50 weight parts of the polyalkylene glycol derivatives.

15 Also, the invention relates to the abovementioned cement additive, wherein the amount of the polycarboxylic acid type copolymers added to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivatives added to cement is 0.0025-0.5 % by weight based on the weight of cement.

20 Further, the invention relates to use of the abovementioned cement additive in high strength concrete.

The invention also relates to the use of the abovementioned cement additive in the formation of pre-formed concrete articles by steam curing.

25 The invention further provides a method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive as hereinabove described.

30 The invention further provides a method of preparation of a concrete mix adapted to be used for the manufacture of articles by steam curing, comprising the incorporation in the mix of a cement additive as hereinabove described.

In a cement additive according to the invention, the monomers (A) are typically compounds according to the abovementioned general formula (1), more specifically, the

compounds in which 1-100 mole of an alkylene oxide is added to an unsaturated alcohol such as 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 2-methyl-3-buten-2-ol. One or more species of unsaturated alcohol may be used.

- 5 Examples of monomers (B) include compounds according to general formula (2), more specifically, for example, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and citraconic acid. One or more species of these may be used.

- 10 Monomers (C) are typically compounds according to general formula (3). Specific examples include unsaturated polyalkylene glycol monoester type monomers such as polyethylene glycol monoesters, polypropylene oxide monoesters, monoesters of polyethylene glycol/polypropylene oxide copolymers, derivatives in which a terminal hydrogen of these glycols is etherified, and the like, such as triethylene glycol monoacrylate, polyethylene glycol (MW 200) monoacrylate, polyethylene glycol (MW 400) monoacrylate, polyethylene glycol (MW 600) monoacrylate, polyethylene glycol (MW 1000) monoacrylate, polyethylene glycol (MW 2000) monoacrylate, polyethylene glycol (MW 4000) monoacrylate, polyethylene glycol (MW 6000) monoacrylate, triethylene glycol monomethacrylate, polyethylene glycol (MW 200) monomethacrylate, polyethylene glycol (MW 400) monomethacrylate, polyethylene glycol (MW 600) monomethacrylate, polyethylene glycol (MW 1000) monomethacrylate, polyethylene glycol (MW 2000) monomethacrylate, polyethylene glycol (MW 4000) monomethacrylate and polyethylene glycol (MW 6000) monomethacrylate, and one or more species of these may be used.

- 25 The monomers (D) are typically compounds according to general formula (4), specific examples including unsaturated polyalkylene glycol diester type monomers and/or styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid alkyl esters (alkyl of C₂₂ maximum), methacrylic acid alkyl ester (alkyl of C₂₂ maximum), maleic anhydride, maleic acid monoesters (alkyl of C₂₂ maximum), and/or alkylene glycol of C₃ maximum and 1-300 alkylene glycol units, maleic acid diester (alkyl of C₂₂ maximum and /or alkylene glycol of C₃ maximum and 1-300 alkylene glycol units, vinyl acetate, acrylamide and acrylamide methylpropansulfonic acid and/or the salts thereof.

Specific examples include styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid butyl ester, methacrylic acid methyl ester, methacrylic acid ethyl ester, methacrylic acid butyl ester, maleic anhydride, maleic acid methyl monoester, maleic acid ethyl monoester, maleic acid methyl diester, maleic acid ethyl diester, vinyl acetate, acrylamide, acrylamide methylpropansulfonic acid and/or the salts thereof, methallyl sulfonic acid and/or the salts thereof. One or more species of these may be used.

Specific non-limiting examples of polycarboxylic acid type copolymers are those described in JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858.

The composition ratio of the monomers (A) and (B) in the polycarboxylic acid type copolymers in the invention to total amount of the monomers is preferably 30-100 mole %, and the average molecular weight is preferably 3,000-100,000.

In the polyalkylene glycol derivatives of the invention, the average molecular weight is 1,000-150,000, preferably 1,000-100,000, more preferably 4,000-50,000, the alkylene is one or more C₂-C₄ species, and it may be block or random in the case of 2 or more species, the terminal groups of polyalkylene glycol are hydrogen, C₁₈ maximum alkyl or phenyl groups.

In a cement additive of the invention, the preferred proportions are 100 weight parts of polycarboxylic acid type copolymers and 5-50 weight parts of polyalkylene glycol derivatives.

A cement additive of the invention is preferably used in such a quantity that polycarboxylic acid type copolymers are present in the proportion 0.05-1.0 % by weight based on cement weight and polyalkylene glycol derivatives are present in the proportion 0.0025-0.5 % by weight based on cement weight. However, the amount of the cement additive according to the invention to be used can be appropriately determined according to a cement composition used, it basically being the amount which is necessary to attain the desired strength development and improved time to form removal after steam curing,

and it is possible that suitable proportions outside these limits may be found.

A cement additive according to the invention may be used for stiff consistency concrete, plastic concrete, high fluidity concrete, high strength concrete, cement paste as
5 generally used, mortar, grout, concrete and the like, although the beneficial effects of the invention are most noticeable in high strength concrete in which the water/cement ratio is low.

A cement additive according to the invention may be mixed, if desired, with other
10 additives to expand its versatility. Typical examples of other additives are conventional water-reducing agents (lignosulfonate, oxycarboxylate, polyalkylsulfonate, polycarboxylate), air content-regulating agents, drying shrinkage reducing agents, accelerators, retarders, foaming agents, anti-foaming agents, anti-rust agents, set acceleration agents, high early-strengthening agents, efflorescence-inhibiting agents,
15 bleeding inhibitors, pumping aids, and water-soluble polymers.

A cement additive according to the invention exhibits a high dispersing ability of a degree never obtained by use only of polycarboxylic acid-type copolymers to various concretes such as ordinary concrete, high strength concrete and steam curing concrete.
20 Without restricting the scope of the invention in any way, it is believed that this is the result of a synergistic effect of the polycarboxylic acid type copolymers and the polyalkylene glycol derivatives. It both enhances the fluidity of concrete and maintains this fluidity, thereby making it possible to increase the strength development and decrease the time for form removal after steam curing. The latter is particularly valuable in that it
25 permits economies such as the reduction of time spent in a form used and the reduction of defects in concrete products manufactured in a concrete factory.

The invention is now further illustrated by the following non-limiting examples wherein are used the cement additives containing polycarboxylic acid type copolymers and
30 polyalkylene glycol derivatives according to the invention.

Examples

The compositions of the polycarboxylic acid type copolymers in the cement

additives used in the examples and in the comparative examples are shown in Table 1. Said polycarboxylic acid type copolymers can be obtained by known polymerization methods described in, for example, JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858. The polyalkylene glycol derivatives in the
5 cement additives used in the examples and in the comparative examples are also shown in Table 2.

In order to illustrate the effect of these cement additives, the concrete compositions (shown in Table 3) are designed to have slump of 18.5 ± 1 cm and air content 4.5%. The
10 total quantity of materials in each case is 80 litres, and all the materials are added to a 100 litre pan-type forced mixing mixer, and mixed for 120 sec. to give the concrete compositions. The concrete compositions thus obtained are measured for slump, air content, setting time and compressive strength. Further, the compressive strength in the case of accelerating the appearance of strength by steam curing was measured.

15

- 1) Slump: measured according to JIS A 1101,
- 2) Air content: measured according to JIS A 1128,
- 3) Setting time: measured according to JIS A 6204 Supplement 1,
- 4) Compressive strength

20

Ordinary curing: measured according to JIS A 1108,

Steam curing: the sample is pre-cured at 20°C for 2 hr, then warmed to 65°C in 2 hrs 30 min, kept at 65°C for 4 hrs. After allowing to cool to 20°C over 4 hrs, the testing is carried out according to JIS A 1108.

25

(Materials used)

Mixing water: tap water,

Cement: ordinary portland cement (density 3.16 g/cm^3),

Fine aggregate: Oi River pit sand (specific gravity 2.59, FM=2.74),

Coarse aggregate: Oume crushed stone (specific gravity 2.65, MS[median size?]=20mm).

30

The results of the above measurement are shown in Table 4. In the Table, the examples 1-13 and the comparative examples 1-4 are for the results obtained from the ordinary cement, and the examples 14, 15 and the comparative examples 5, 6 are those

obtained from the high strength concrete.

The examples 1-7 show the cases in which the type of the polycarboxylic acid type copolymers is changed, and the examples 1 and 8-13 are the cases in which the type of the polyalkylene glycol derivatives is changed.

The comparative examples 1 and 5 show the cases in which a polyalkylene glycol derivative is not used, and the comparative examples 2-4 and 6 are the cases in which compounds other than the polycarboxylic acid type copolymers in the invention are used.

As is evident from the comparison between the comparative example 1 and the examples 1-13, and from the comparison between the comparative example 5 and the examples 14 and 15, the ordinary concrete and the high strength concrete, in which the cement additives together with the polyalkylene glycol derivatives of the invention are used, both show a tendency to accelerate setting, whereby the slump values are large (fluidity) and their slump lowering over 60 min is small (high flowability), demonstrating a preferable compressive strength both for ordinary curing and steam curing.

The comparative examples 2-4 and 6 are those in which compounds other than the polycarboxylic acid type copolymers in the invention are used, though in these examples the development of compressive strength is not sufficient, because there is demonstrated a retardation of setting.

Table 1

Type of Polycarboxylic Acid-type copolymer	Type of monomer and composition ratio											Average Molecular Weight
	Monomer (A)			Monomer (B)			Monomer (C)			Monomer (D)		
	Mole ratio (%)	Type	AG No.	Mole ratio (%)	Type	Mole ratio (%)	Type	Mole ratio (%)	Type	Mole ratio (%)	Type	
PCA-1	1.5	Polyethylene glycol mono-vinyl ether	50	1	Maleic acid	-	-	-	-	-	-	20000
PCA-2	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	50	1	Maleic acid	-	-	-	-	-	-	30000
PCA-3	1.5	Polyethylene glycol mono-vinyl ether	50	1	Maleic acid	0.2	Polyethylene glycol maleic acid ester	75	-	-	-	35000
PCA-4	1.5	Polyethylene glycol polypropylene glycol allyl ether	50	1	Maleic acid	0.3	Polyethylene glycol maleic acid ester	25	0.1	Maleic anhydride	-	24000
PCA-5	1.5	Polyethylene glycol allyl ether	12	1	Maleic acid	-	-	-	0.2	Styrene	-	32000
PCA-6	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	25	1	Acrylic acid	-	-	-	0.2	Acrylamide methypropan sulfonic acid	-	27000
PCA-7	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	75	1	Acrylic acid	-	-	-	0.2	Polyethylene glycol dimethacrylic acid ester	-	75000
P-1	1	2-Methyl 2-propen-1-ol alkylene oxide adduct	50	1	Maleic acid	2	Polyethylene glycol maleic acid ester	25	-	-	-	30000
P-2	1	Polyalkylene glycol monovinyl ether	50	1	Maleic acid	2	Polyethylene glycol methacrylic acid ester	25	-	-	-	28000
P-3	-	-	-	1	Acrylic acid	2	Polyethylene glycol methacrylic acid ester	100	-	-	-	28000

Table 2

Sample mark	Component name of polyalkylene glycol	Average molecular weight
PAG-1	Polyethylene glycol	4000
PAG-2	Polyethylene glycol	6000
PAG-3	Polyethylene glycol	10000
PAG-4	Polyethylene glycol	20000
PAG-5	Polyethylene glycol	50000
PAG-6	Polyethylene glycol-polypropylene glycol block polymer	4000
PAG-7	Polyethylene glycol oleic acid ester	5000

5 Table 3 (Blend)

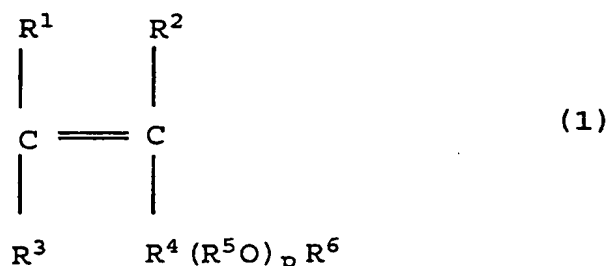
Type of Concrete	W/C (%)	s/a (%)	Unit amount (Kg/m ³)			
			W	C	S	G
Ordinary Concrete	50	46	160	320	823	993
High-strength concrete	35.6	44	160	450	741	968

Table 4 (Concrete test)

	Type of blend	No.	Polycarboxylic acid type copolymer		PAG		Slump (cm)		Air content (%)		Setting time (min)		Compressive strength (N/mm ²)	
			Type	Amount added (wt%)	Type	Amount added (wt%)	Just after	60 min later	Just after	60 min later	Start	End	Standard curing age 3 days	steam curing age 7 hrs
Example	Ordinary Concrete	1	PCA-1	0.2	PAG-4	0.03	19.0	15.0	4.5	4.5	355	450	25.0	27.6
		2	PCA-2	0.2	PAG-4	0.03	18.5	16.0	4.4	4.4	350	450	25.4	27.9
		3	PCA-3	0.2	PAG-4	0.03	18.0	15.5	4.6	4.5	355	450	25.2	27.6
		4	PCA-4	0.2	PAG-4	0.03	18.5	19.0	4.4	4.5	355	460	24.5	27.1
		5	PCA-5	0.2	PAG-4	0.03	18.0	15.0	4.4	4.3	355	450	25.6	28.3
		6	PCA-6	0.2	PAG-4	0.03	18.0	15.0	4.6	4.5	355	450	25.2	27.4
		7	PCA-7	0.2	PAG-4	0.03	18.5	18.5	4.3	4.4	355	450	24.1	29.2
		8	PCA-1	0.2	PAG-1	0.05	18.0	15.0	4.2	4.3	355	450	25.2	28.4
		9	PCA-1	0.2	PAG-2	0.05	18.0	15.0	4.4	4.5	355	450	25.6	28.3
		10	PCA-1	0.2	PAG-3	0.05	18.5	15.0	4.5	4.6	355	450	25.4	28.3
		11	PCA-1	0.2	PAG-5	0.05	18.0	15.0	4.5	4.3	355	450	25.3	28.3
		12	PCA-1	0.2	PAG-6	0.03	18.5	15.0	4.6	4.4	355	450	26.7	28.4
		13	PCA-1	0.2	PAG-7	0.03	18.5	15.0	4.6	4.5	355	450	26.7	27.1
Comparative Example	High Strength Concrete	14	PCA-1	0.2	PAG-4	0.03	19.0	15.0	4.5	4.5	300	395	36.4	39.1
		15	PCA-2	0.2	PAG-4	0.03	18.5	16.0	4.4	4.4	305	390	36.2	39.0
	Ordinary Concrete	1	PCA-1	0.3	-	-	17.5	6.0	4.4	4.0	380	485	20.4	23.4
		2	P-1	0.2	PAG-4	0.05	18.5	14.5	4.3	5.7	355	450	22.4	23.5
		3	P-2	0.2	PAG-4	0.05	19.0	13.5	4.5	5.9	355	455	22.6	23.8
		4	P-3	0.2	PAG-4	0.05	18.5	14.0	4.5	5.9	380	470	22.7	23.5
	High strength concrete	5	PCA-1	0.3	-	-	13.0	6.0	4.4	4.0	340	495	31.0	35.2
		6	P-3	0.3	PAG-4	0.05	18.5	14.0	4.5	5.9	350	445	31.5	36.0

Claims

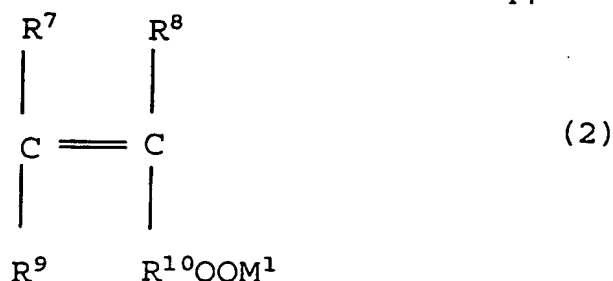
1. A cement additive comprising a polycarboxylic acid type copolymer and/or a salt thereof and a polyalkylene glycol derivative, wherein said polycarboxylic acid type copolymer contains at least one species of copolymer derived from at least an unsaturated polyalkylene glycol ether type monomer (A) and an unsaturated mono- or dicarboxylic acid type monomer (B) as its monomer component.
2. A cement additive according to claim 1, wherein the polycarboxylic acid type copolymer is additionally derived from an unsaturated polyalkylene glycol ester type monomer (C) and/or a monomer (D), which is copolymerizable with the above monomers (A) and (B), or with the monomers (A), (B) and (C).
3. A cement additive according to claim 1 or 2, wherein the monomer (A) is a compound according to general formula (1):



- wherein R^1 , R^2 and R^3 are each independently hydrogen or methyl, provided that not all are methyl; R^4 is $-\text{CH}_2\text{O}-$, $-(\text{CH}_2)_2\text{O}-$, $-\text{C}(\text{CH}_3)_2\text{O}-$ or $-\text{O}-$; the total carbon number of R^1 , R^2 , R^3 and R^4 is 3; $R^5\text{O}$ is one or more species of C_2 - C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; R^6 is hydrogen or a C_1 - C_{22} alkyl, phenyl or C_1 - C_{18} alkylphenyl group; p is an integer from on average 1 to 100,

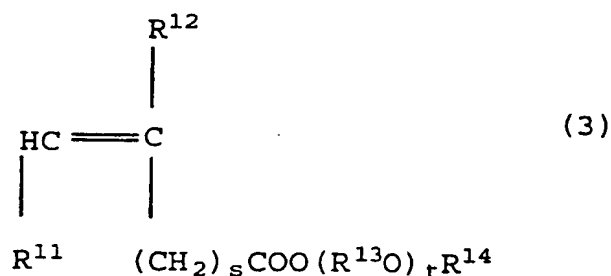
the monomer (B) is a compound according to general formula (2):

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wherein R^7 and R^8 are each independently hydrogen or methyl; R^9 is hydrogen, methyl or $-(CH_2)_qCOOM^2$; R^{10} is $-(CH_2)_r-$; q and r are each independently an integer from 0 to 2; M^1 and M^2 are a monovalent metal, a divalent metal, ammonium or an organic amine;

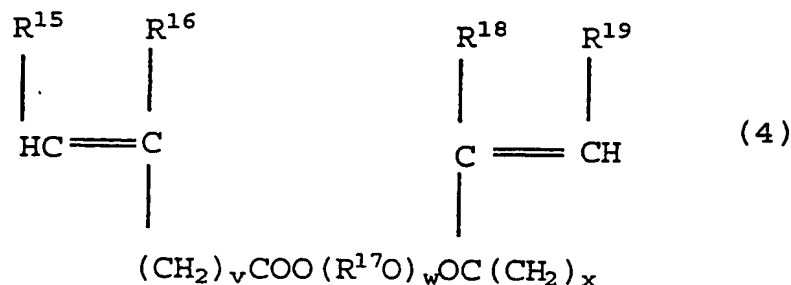
the monomer (C) is a compound according to general formula (3):



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wherein R^{11} and R^{12} are each independently hydrogen, methyl or $(CH_2)_uCOOM^3$, u is an integer from 0 to 2, M^3 is a monovalent metal, a divalent metal, ammonium or an organic amine; $R^{13}O$ is one or more species of C_2 - C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; R^{14} is a C_1 - C_{22} hydrogen or an alkyl, phenyl or C_1 - C_{22} alkylphenyl group; s is an integer from 0 to 2; t is an integer an average from 1 to 300; and

the monomer (D) is a compound according to the following general formula (4):



wherein R^{15} , R^{16} , R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; $R^{17}O$ is one or more species of C_2 - C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

4. A cement additive according to any one of claims 1-3, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid type copolymer are 30-100 mole % based on the total mole amount of their monomers, and the average molecular weight of said polycarboxylic acid type copolymer is from 3,000 to 100,000.

5. A cement additive according to any one of claims 1-3, wherein the average molecular weight of the polyalkylene glycol derivative is from 1,000 to 100,000, and in which the alkylene is one or more C_2 - C_4 species, and the terminal group of the polyalkylene glycol is hydrogen, a C_1 - C_{18} alkyl group or a phenyl group.

6. A cement additive according to any one of claims 1-5, containing 100 weight parts of the polycarboxylic acid type copolymer and 5-50 weight parts of the polyalkylene glycol derivative in the mixing proportion.

7. A cement additive according to any one of claims 1-6, wherein the amount used in a cementitious composition is such that the amount of polycarboxylic acid type copolymer to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivative to cement is 0.0025-0.5 % by weight based on the weight of cement.

8. A high strength concrete mix, comprising a cement additive according to any one of claims 1-7.

9. A concrete mix for the production of articles by steam curing, comprising a cement additive according to any one of claims 1-7.

10. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.

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11. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/01275

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B24/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 850 894 A (NIPPON CATALYTIC CHEM IND) 1 July 1998 (1998-07-01) page 2, line 33 -page 6, line 49 page 9, line 33 - line 44	1-11
A	DE 41 42 388 A (SANDOZ AG) 2 July 1992 (1992-07-02) page 2, line 5 -page 3, line 57	1,8,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

16 May 2000

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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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